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(74) Agent: BORDAS, Carol, I.; Seagate Technology LLC, 1251 Waterfront Place, Pittsburgh, PA 15222 (US).

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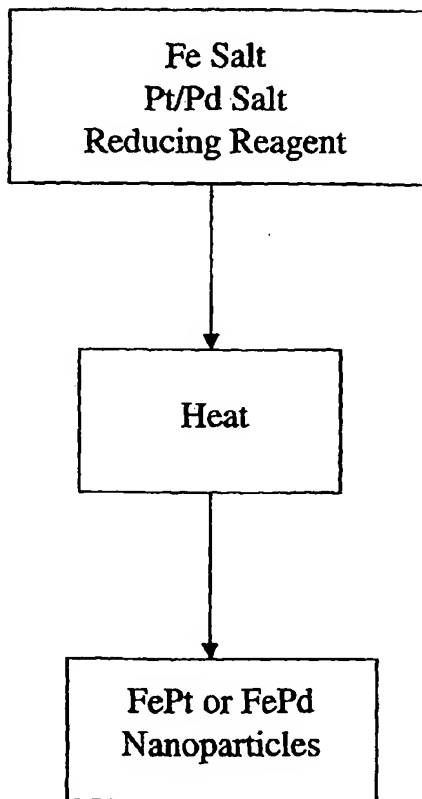
(71) Applicant: SEAGATE TECHNOLOGY LLC [US/US]; 920 Disc Drive, Scotts Valley, CA 95066 (US).

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(72) Inventors: LIU, Chao; C811, McKnight Circle, Pittsburgh, PA 15237 (US). YANG, Xiaomin; 1802 Gibson Drive, Sewickley, PA 15143 (US). WELLER, Dieter, K.; 7019 Oak Park Drive, Gibsonia, PA 15044 (US).

[Continued on next page]

(54) Title: SYNTHESIS OF IRON-BASED ALLOY NANOPARTICLES



(57) Abstract: A method of forming iron-based alloy nanoparticles is disclosed. A solution containing iron salt, noble metal salt and a reducing reagent is heated, resulting in the precipitation of monodispersed nanoparticles such as FePt and FePd. The solution may also include a surfactant. After deposition, the iron-based alloy nanoparticles may be annealed in order to produce the desired crystal structure and magnetic properties. The annealed nanoparticles may comprise FePt having an L1₀ crystal structure and high magnetic coercivity. The magnetic iron-based nanoparticles are suitable for use in applications such as magnetic recording media, permanent magnet materials and magneto-transport systems.

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**Declaration under Rule 4.17:**

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European

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SYNTHESIS OF IRON-BASED ALLOY NANOPARTICLES

FIELD OF THE INVENTION

The present invention relates to iron-based nanoparticles, and more particularly relates to a method of synthesizing FePt and FePd nanoparticles from iron salts and Pt or Pd salts. The FePt and FePd nanoparticles are useful in applications such as magnetic recording media, permanent magnet materials and magneto-transport systems.

BACKGROUND INFORMATION

The synthesis of Fe-based alloy nanoparticles with controlled size and size distribution has been explored. Colloidal chemistry synthesis has been investigated as a method of making monodispersed nanoparticles. Conventional solution phase chemical synthesis is based on thermal decomposition of iron pentacarbonyl and reduction of a metal salt simultaneously in a solution in the presence of surfactant molecules. However, iron pentacarbonyl is highly toxic and highly flammable at room temperature. In addition to safety concerns, the amount of iron pentacarbonyl is difficult to control, which is essential to the chemical composition of the Fe-based alloy. The present invention provides an alternative method for synthesizing Fe-based alloy nanoparticles without using iron pentacarbonyl.

SUMMARY OF THE INVENTION

An aspect of the present invention is to provide a method of making iron alloy nanoparticles. The method comprises providing a solution comprising at least one iron salt, at least one noble metal salt comprising a platinum salt and/or a palladium salt, and at least one reducing reagent; heating the solution; and recovering iron alloy nanoparticles comprising Fe and the noble metal.

Another aspect of the present invention is to provide a method of making a magnetic film such as a magnetic recording medium. The method comprises providing a solution comprising at least one iron salt, at least one noble metal salt comprising a platinum salt and/or a palladium salt, and at least one reducing reagent; heating the solution; depositing iron alloy nanoparticles from the heated solution on a substrate; and annealing the iron alloy nanoparticles.

A further aspect of the present invention is to provide iron alloy nanoparticles comprising Fe from an iron salt, and a noble metal from a noble metal salt, wherein the noble metal comprises Pt and/or Pd.

These and other aspects of the present invention will be more apparent from the following description.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a flow diagram illustrating a process for forming Fe-based alloy nanoparticles in accordance with an embodiment of the present invention.

Fig. 2 is a flow diagram illustrating a process for forming Fe-based alloy nanoparticles in accordance with another embodiment of the present invention.

Fig. 3 is a bright field TEM image of monodispersed FePt nanoparticles self-organized into a superlattice produced in accordance with an embodiment of the present invention.

Fig. 4 is a HRTEM image of as-prepared FePt nanoparticles produced in accordance with an embodiment of the present invention.

Fig. 5 is an X-ray diffraction pattern demonstrating the presence of the $L1_0$ crystal phase in an annealed FePt nanoparticle film produced in accordance with an embodiment of the present invention.

DETAILED DESCRIPTION

Fig. 1 illustrates the production of Fe-based alloy nanoparticles in accordance with an embodiment of the present invention. A solution including an iron salt, a noble metal salt, and a reducing reagent is provided. The solution is heated in order to precipitate nanoparticles comprising an alloy of Fe and the noble metal. In one embodiment, surfactant molecules and/or other ligands are used to provide repulsive forces to prevent agglomeration of the particles.

Suitable iron salts include Fe(II) acetylacetonate, Fe(III) acetylacetonate, anhydrous Fe(II) chloride, anhydrous Fe(III) chloride, Fe(III) ethoxide, anhydrous Fe(II) acetate, anhydrous Fe(II) bromide, anhydrous Fe(III) bromide, Fe(III) i-propoxide and/or Fe(II) stearate. For example, the iron salt may comprise Fe(II) acetylacetonate and/or Fe(III) acetylacetonate. The iron salt concentration is typically from about 0.001 Mol/L to about 0.1 Mol/L in the solution.

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The noble metal of the Fe-based alloy is preferably Pt and/or Pd, and may be provided from salts such as Pt(II) acetylacetonate, Pd(II) acetylacetonate, Pt(II) 1,1,1,5,5,5-hexafluoro2,4-pentanedionate, Pd(II) acetate, Pt(II) chloride and/or Pd(II) chloride. For example, the noble metal salt may comprise Pt(II) acetylacetonate and/or Pt(II) 1,1,1,5,5,5-hexafluoro2,4-pentanedionate, with Pt(II) acetylacetonate being particularly suitable. The noble metal salt concentration is typically from about 0.001 Mol/L to about 0.1 Mol/L in the solution.

The relative amounts of iron salts and noble metal salts may be selected based upon the desired final alloy composition. For example, the iron and noble metal salt amounts may be chosen based upon the desired atomic ratio of Fe:Pt in the alloy. In accordance with an embodiment of the present invention, the chemical composition can be readily controlled by the relative amounts of Fe(II) acetylacetonate (or Fe(III) acetylacetonate) and Pt(II) acetylacetonate.

Suitable reducing reagents include 1,2-hexadecanediol, 1,2-dodecanediol and/or 1,2-octanediol. For example, the reducing reagent may comprise 1,2-hexadecanediol. The reducing reagent concentration is typically from about 0.005 Mol/L to about 0.5 Mol/L in the solution.

The process of the present invention reduces the iron salt together with the other Pt or Pd component salts for the Fe-based alloy system. Such salts in solid powder form are relatively easy to handle, and the amount of chemicals added can be more accurately controlled. The reducing reagent, such as 1,2-hexadecanediol with large hydrocarbon chains, may be chemically stable at room temperature, but may be a very strong reducing reagent under high temperature.

The solution may further include a surfactant such as oleic acid, oleylamine, trioctylphosphine oxide (TOPO), hexanoic acid, dodecyl-benzene sodium sulfate and/or sodium dodecylsulfonate. For example, oleic acid and/or oleylamine may be particularly useful. The surfactant concentration is typically from about 0.0001 Mol/L to about 0.2 Mol/L in the solution.

The solution may include a solvent with high boiling point and adequate solubility for the Fe and the noble metal salts. For example, the solvent can be octyl ether and/or phenyl ether.

In addition to the Fe and noble metal salts, reducing reagent, surfactant and solvent, the solution may optionally include other ingredients such as Co(II)

acetylacetonate, Ag(I) acetate, Ni(II) acetylacetonate, Cu(II) acetylacetonate and/or Au(III) chloride in a total chemical amount of up to about 90 percent to replace Fe and/or noble metal salts in the solution.

The solution may be heated to a temperature of at least about 240°C. For example, the solution may be heated to a temperature from about 250°C to about 300°C.

Upon deposition, the iron alloy nanoparticles typically comprise from about 5 to about 95 atomic percent Fe, and from about 5 to about 95 atomic percent noble metal. For example, the iron alloy nanoparticles may comprise from about 25 to about 75 atomic percent Fe, and from about 25 to about 75 atomic percent Pt and/or Pd.

The iron alloy nanoparticles typically have an average size of from about 2 to about 15 nm, for example, from about 3 to about 10 nm. The iron alloy nanoparticles are substantially monodispersed. As used herein, the term "monodispersed" means that the standard deviation of diameter over average diameter is less than 10 percent. The iron alloy nanoparticles may be deposited in the form of a superlattice on any suitable substrate such as a thermally oxidized Si substrate, Si₃N₄, glass or the like. The as-deposited nanoparticles may typically be chemically disordered. For example, as-deposited FePt may comprise a disordered face-center-cubic phase.

After deposition, the iron alloy nanoparticles may be annealed. Suitable annealing temperatures may range from about 450 to about 800°C, typically from about 500 to about 650°C. Upon annealing, the nanoparticles have a crystalline microstructure. For example, annealed FePt nanoparticles may have an L1₀ structure.

The annealed iron alloy nanoparticles may have a room temperature coercivity of at least 300 Oe, typically greater than about 500 Oe. FePt alloys are particularly suitable for use in permanent magnets due to their large uniaxial magnetocrystalline anisotropy energy.

Another synthesis process to obtain monodispersed Fe-based alloy nanoparticles is shown in Fig. 2. The process includes: mixing the iron salt and Pt/Pd salt precursors into the solvent together with the reducing reagent and surfactant molecules; heating inside the reaction vessel and reflux; and performing a standard size selective precipitation process to obtain the monodispersed particles, e.g., if the size distribution is more than 10 percent.

As a particular example, monodispersed FePt nanoparticles may be synthesized using 0.0025 mol 1,2-hexadecanediol as the reducing agent, 20.0 ml octyl

ether as the solvent, 0.001 mol oleic acid and oleylamine as the surfactant molecules, 0.0005 mol Fe(II) acetylacetonate (or Fe(III) acetylacetonate) and 0.0005 mol Pt(II) acetylacetonate as the salts for Fe and Pt, respectively. The solution is heated to refluxing at 286°C and held at this temperature for 30 minutes. At such high temperature the metal cations are reduced. While not intending to be bound by any particular theory, a possible mechanism is that one molecule of 1,2-hexadecanediol loses one molecule of water and becomes a reducing agent, which could be an aldehyde or its isomerization form. The reducing reagent is oxidized by the metal cations, or the metal cations, e.g., Fe(II) (or Fe(III)) and Pt(II), are reduced by the aldehydes. The heat source is then removed and the product solution cooled to room temperature. The solution is then purified using a flocculent such as ethanol, followed by dispersion in an apolar solvent such as hexane.

The monodispersed FePt alloy particles self-organize into the superlattices shown in Figs. 3 and 4. A bright field TEM image of an as-prepared FePt nanoparticle sample, without going through the size selective precipitation process, is shown in Fig. 3. An HRTEM image of a similar sample is shown in Fig. 4. The images show that the particles have uniform lattice fringes across the particles, which may be attributed to good crystallinity of the chemically disordered FCC crystalline phase. Identification of random lattice fringes for FCC FePt (111) and (200) planes indicates that the particles are randomly oriented.

An X-ray diffraction pattern of FePt nanoparticles having an L1₀ crystal structure is shown in Fig. 5. The chemically ordered L1₀ crystalline phase, as shown in Fig. 5, is obtained after annealing at 650°C for 30 minutes using standard rapid thermal annealing techniques. Hysteresis measurements show that the coercivity of the chemically ordered sample is 12.7kOe at room temperature and 23.1kOe at 5K.

Whereas particular embodiments of this invention have been described above for purposes of illustration, it will be evident to those skilled in the art that numerous variations of the details of the present invention may be made without departing from the invention as defined in the appended claims.

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WHAT IS CLAIMED IS:

1. A method of making iron alloy nanoparticles, the method comprising:
providing a solution comprising at least one iron salt, at least one noble metal salt comprising a platinum salt and/or a palladium salt, and at least one reducing reagent;
heating the solution; and
recovering iron alloy nanoparticles comprising Fe and the noble metal.
2. The method of Claim 1, wherein the iron salt comprises Fe(II) acetylacetonate, Fe(III) acetylacetonate, anhydrous Fe(II) chloride, anhydrous Fe(III) chloride, Fe(III) ethoxide, anhydrous Fe(II) acetate, anhydrous Fe(II) bromide, anhydrous Fe(III) bromide, Fe(III) i-propoxide and/or Fe(II) stearate.
3. The method of Claim 1, wherein the iron salt comprises Fe(II) acetylacetonate and/or Fe(III) acetylacetonate.
4. The method of Claim 1, wherein the noble metal salt comprises Pt(II) acetylacetonate, Pd(II) acetylacetonate, Pt(II) 1,1,1,5,5,5-hexafluoro2,4-pentanedionate, Pd(II) acetate, Pt(II) chloride and/or Pd(II) chloride.
5. The method of Claim 1, wherein the noble metal salt comprises Pt(II) acetylacetonate.
6. The method of Claim 1, wherein the noble metal salt comprises Pt(II) 1,1,1,5,5,5-hexafluoro2,4-pentanedionate.
7. The method of Claim 1, wherein the reducing reagent comprises 1,2-hexadecanediol, 1,2-dodecanediol and/or 1,2-octanediol.
8. The method of Claim 1, wherein the reducing reagent comprises 1,2-hexadecanediol.
9. The method of Claim 1, wherein the solution is heated to a temperature of at least 240°C.
10. The method of Claim 1, wherein the solution is heated to a temperature of from about 250 to about 300°C.
11. The method of Claim 1, wherein the iron alloy nanoparticles comprise from about 5 to about 95 atomic percent Fe, and from about 5 to about 95 atomic percent Pt.

12. The method of Claim 1, wherein the iron alloy nanoparticles have an average size of from about 2 to about 15 nm.

13. The method of Claim 1, wherein the iron alloy nanoparticles are monodispersed.

14. The method of Claim 1, wherein the iron alloy nanoparticles are deposited on a substrate in the form of a superlattice.

15. The method of Claim 1, wherein the solution further comprises a surfactant.

16. The method of Claim 15, wherein the surfactant comprises oleic acid, oleylamine, trioctylphosphine oxide, hexanoic acid, dodecyl-benzene sodium sulfate and/or sodium dodecylsulfonate.

17. The method of Claim 15, wherein the surfactant comprises oleic acid and/or oleylamine.

18. The method of Claim 1, wherein the solution comprises a solvent including octyl ether.

19. The method of Claim 1, wherein the solution comprises a solvent including phenyl ether.

20. The method of Claim 1, further comprising annealing the iron alloy nanoparticles.

21. The method of Claim 20, wherein the iron alloy nanoparticles are annealed at a temperature of from about 450 to about 800°C.

22. The method of Claim 20, wherein the annealed iron alloy nanoparticles have an L1₀ crystal structure.

23. The method of Claim 20, wherein the annealed iron alloy nanoparticles have a room temperature coercivity of at least 300 Oe.

24. A method of making a magnetic film, the method comprising:
providing a solution comprising at least one iron salt, at least one noble metal salt comprising a platinum salt and/or a palladium salt, and at least one reducing reagent;

heating the solution;

depositing iron alloy nanoparticles from the heated solution on a substrate; and

annealing the iron alloy nanoparticles.

25. The method of Claim 24, wherein the iron salt comprises Fe(II) acetylacetonate, Fe(III) acetylacetonate, anhydrous Fe(II) chloride, anhydrous Fe(III) chloride, Fe(III) ethoxide, anhydrous Fe(II) acetate, anhydrous Fe(II) bromide, anhydrous Fe(III) bromide, Fe(III) i-propoxide and/or Fe(II) stearate, and the noble metal salt comprises Pt(II) acetylacetonate, Pd(II) acetylacetonate, Pt(II) 1,1,1,5,5,5-hexafluoro2,4-pentanedionate, Pd(II) acetate, Pt(II) chloride and/or Pd(II) chloride.

26. The method of Claim 24, wherein the deposited iron alloy nanoparticles are in the form of a monodispersed superlattice.

27. Iron alloy nanoparticles comprising:
Fe from an iron salt; and
a noble metal from a noble metal salt, wherein the noble metal comprises Pt and/or Pd.

28. The iron alloy nanoparticles of Claim 27, wherein the nanoparticles are in the form of a monodispersed superlattice.

29. The iron alloy nanoparticles of Claim 27, wherein the deposited iron alloy nanoparticles comprise from about 5 to about 95 atomic percent Fe and from about 5 to about 95 atomic percent Pt.

30. The iron alloy nanoparticles of Claim 27, wherein the annealed iron alloy nanoparticles have a room temperature coercivity of at least 300 Oe.

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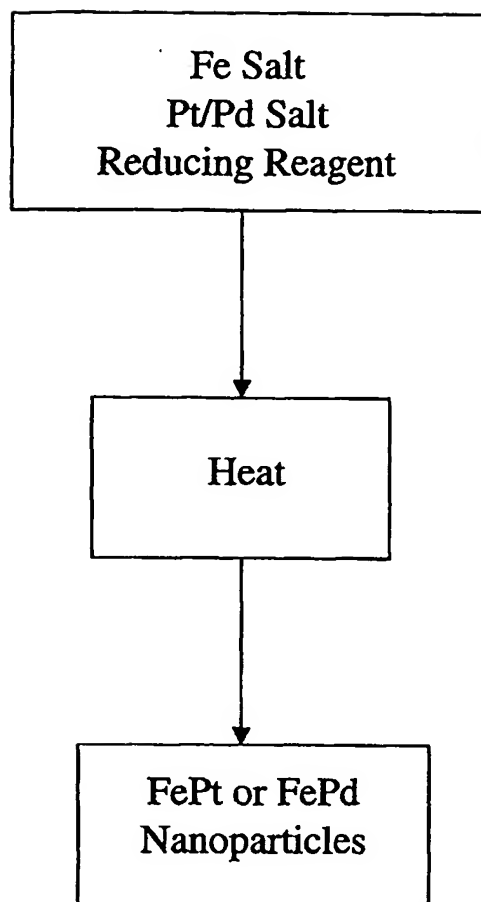


FIG. 1

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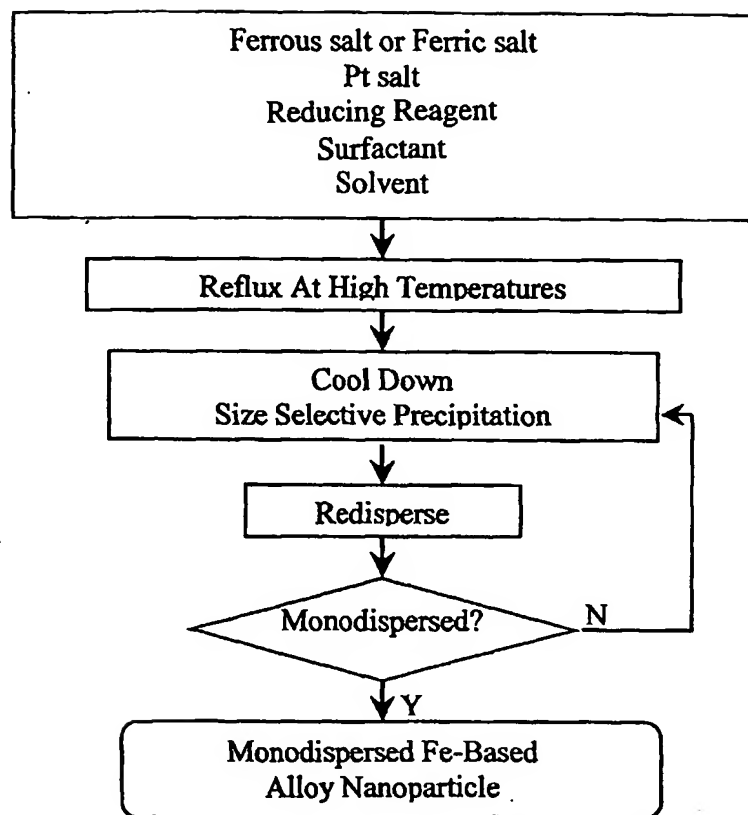


FIG. 2

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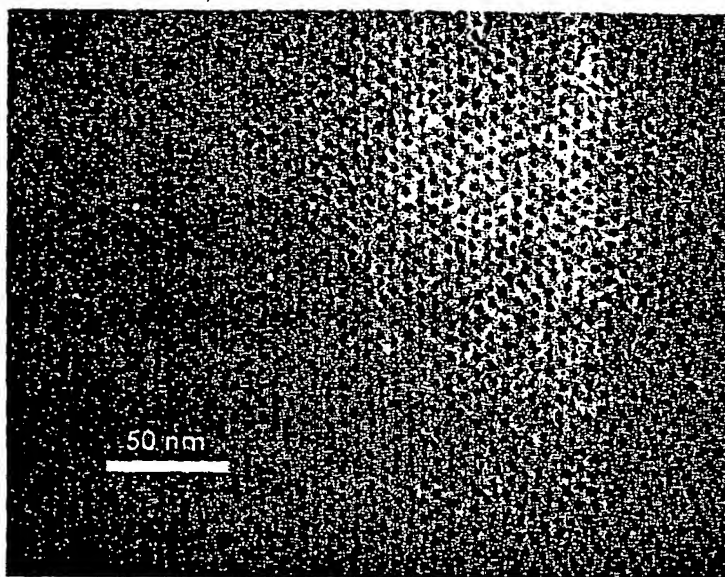


FIG. 3

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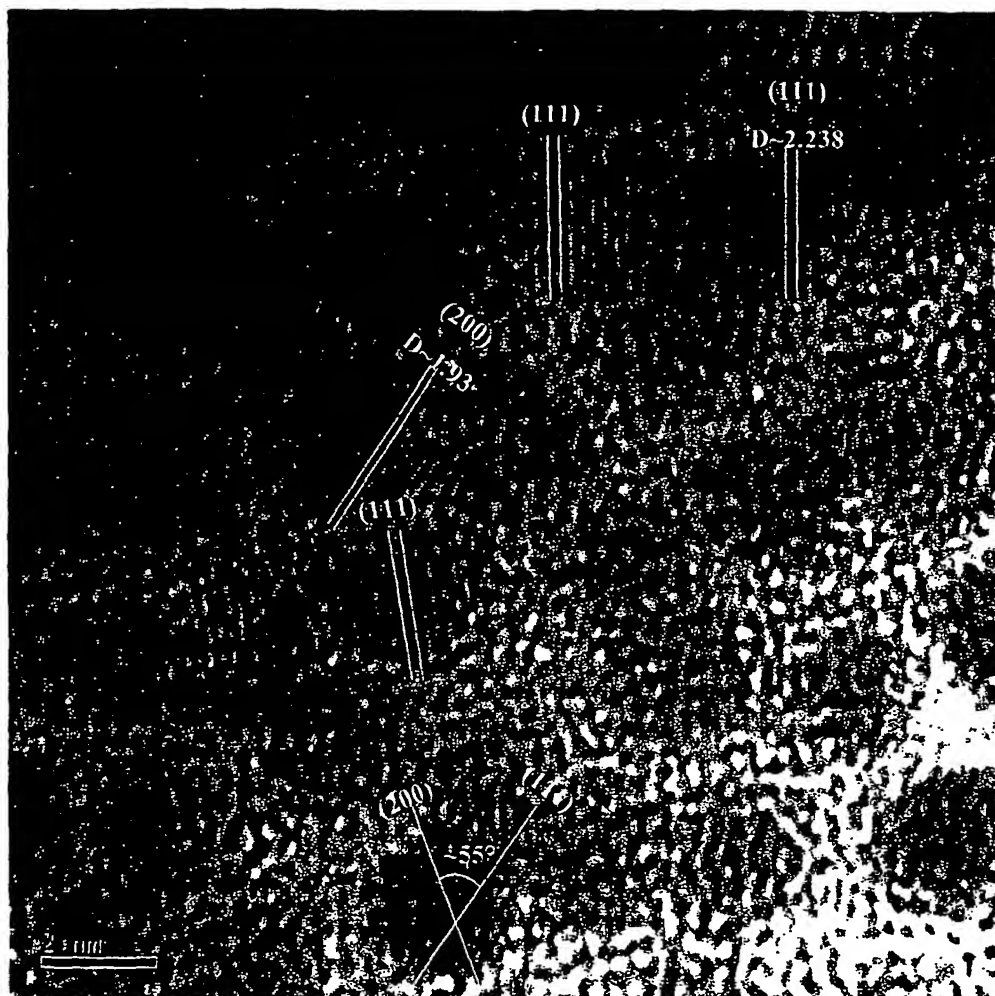
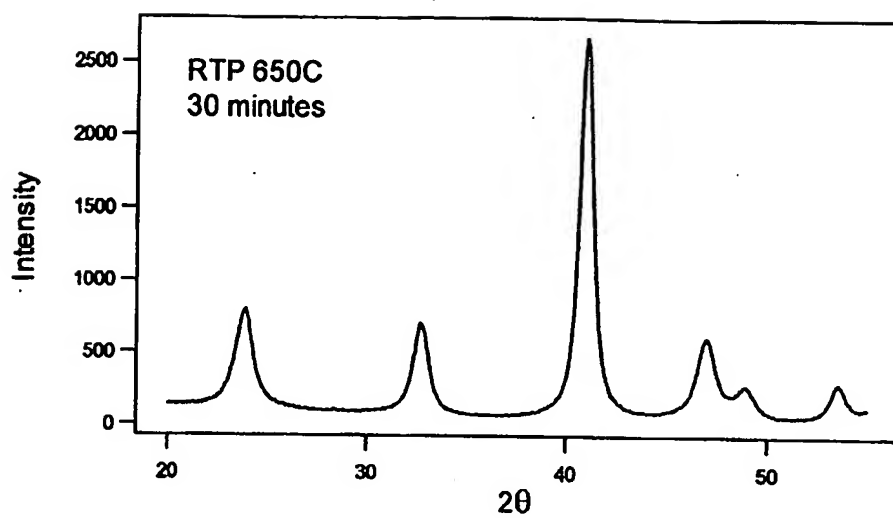


FIG. 4

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**FIG. 5**

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 03/17005

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B22F9/24 C22C33/02 B22F1/00 C23C18/50 G11B5/84

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B22F C23C G11B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 977 212 A (IBM) 2 February 2000 (2000-02-02) abstract; claims 1,15	1,24,27
X	US 2002/018896 A1 (EMOTO MAKIKO ET AL) 14 February 2002 (2002-02-14) paragraph '0029! - paragraph '0030!	1,24,27
X	US 4 629 709 A (BELLONI COFLER JACQUELINE ET AL) 16 December 1986 (1986-12-16) column 3, line 41 - line 60; claims	1,24,27
	-/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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A document defining the general state of the art which is not considered to be of particular relevance

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Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search

20 January 2004

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27/01/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Alvazzi Delfrate, M

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/17005

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SUN S ET AL: "MONODISPERSE FEPT NONOPARTICLES AND FERROMAGNETIC FEPT NANOCRYSTAL SUPERLATTICES" SCIENCE, AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE,, US, vol. 287, no. 5460, 17 March 2000 (2000-03-17), pages 1989-1991, XP001089844 ISSN: 0036-8075	1
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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